

RI 9535

PLEASE DO NOT REMOVE FROM LIBRARY

FEB 22 1995

Leaching of Petroleum Catalysts With Cyanide for Palladium Recovery

By P. L. Sibrell and G. B. Atkinson

U.S. Department of the Interior
Mission Statement

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally-owned public lands and natural resources. This includes fostering sound use of our land and water resources; protecting our fish, wildlife, and biological diversity; preserving the environmental and cultural values of our national parks and historical places; and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to ensure that their development is in the best interests of all our people by encouraging stewardship and citizen participation in their care. The Department also has a major responsibility for American Indian reservation communities and for people who live in island territories under U.S. administration.

Report of Investigations 9535

Leaching of Petroleum Catalysts With Cyanide for Palladium Recovery

By P. L. Sibrell and G. B. Atkinson

**UNITED STATES DEPARTMENT OF THE INTERIOR
Bruce Babbitt, Secretary**

**BUREAU OF MINES
Rhea L. Graham, Director**

International Standard Serial Number
ISSN 1066-5552

CONTENTS

Page

Abstract	1
Introduction	2
Experimental	2
Materials	2
Procedures	2
Results and discussion	3
Leaching tests	3
Solid waste characterization analysis	6
Pd recovery from solution	6
Conclusions	8
Acknowledgment	8
References	9

TABLES

1. Petroleum catalyst sample characterization	3
2. Leaching results—catalyst sample 1	4
3. Autoclave leaching results—catalyst sample 2	6
4. Autoclave leaching results—catalyst sample 3	6
5. Toxicity characteristics test results, Federal TCLP procedure	7
6. Toxicity characteristics test results, California WET procedure	7
7. Precipitation of Pd from leach solution	8

UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

Metric Units

g	gram	mL	milliliter
g/t	gram per metric ton	mm	millimeter
h	hour	MPa	megapascal
L	liter	pct	percent
<u>M</u>	molar mass	ppm	part per million
m²/g	square meter per gram	°C	degree Celsius
mg/L	milligram per liter		

U.S. Customary Unit

psia **pound per square inch, absolute**

LEACHING OF PETROLEUM CATALYSTS WITH CYANIDE FOR PALLADIUM RECOVERY

By P. L. Sibrell¹ and G. B. Atkinson²

ABSTRACT

The U.S. Bureau of Mines has tested cyanide leaching for recovery of palladium (Pd) from spent petroleum processing catalysts. Three different catalyst samples were supplied by a spent-catalyst processor. These catalysts consisted of a zeolite base and contained 0.4 to 0.7 pct Pd. During alkaline cyanide leaching, the catalysts exhibited ion-exchange properties due to their zeolite matrices. Hydrogen ions were released from the zeolite in exchange for sodium ions in solution, resulting in a significant decrease in solution pH. This could present a safety hazard because of the potential for release of toxic hydrogen cyanide gas. A pretreatment step where the catalysts were contacted with a 1.0M sodium hydroxide solution was found to prevent the pH shift from occurring. Following the sodium hydroxide pretreatment, two stages of leaching at 160 °C with solution containing 1 pct sodium cyanide and 0.1M sodium hydroxide gave at least 75 and up to 95 pct Pd recovery. The Pd was quantitatively recovered from the leach solution by thermal decomposition in an autoclave at 250 °C for 1 h. The Pd content of the precipitate was over 50 pct. Thermal decomposition also decreased the total cyanide content of the barren solution to less than 0.2 mg/L. The catalyst leach residues passed the Federal Toxicity Characteristic Leaching Procedure and the California Waste Extraction Test, indicating that landfill disposal of the leach residues would be acceptable.

¹Chemical engineer.

²Supervisory chemist.

Reno Research Center, U.S. Bureau of Mines, Reno, NV.

INTRODUCTION

Platinum-group metal (PGM) catalysts are often used in the processing of crude petroleum to produce refined gasoline and other products. Some of the typical uses for catalysts are in fluid catalytic cracking, reforming, and isomerization processes (1).³ The catalysts can be regenerated a number of times, but eventually, they become poisoned and must be discarded. The high PGM content of the catalysts is an incentive for recycling, and petroleum processors usually contract with reprocessing specialists to process their spent catalysts. These companies recover the PGM content of the spent catalysts by acid leaching and other processes. The acid leaching flowsheet has several drawbacks, such as the corrosive nature of process solutions and the necessity for disposal of waste acid and other products. One of the major byproducts is alum, generated from the aluminum content of the catalyst base. This can be used in water treatment and sometimes can be a salable product. However, if the alum is not marketable, it can be a considerable waste disposal problem because of the large volume generated. Other processes used to recover the PGM include high-temperature chlorination and plasma furnace melting. However, dust and vapor emissions from these processes can be significant. A more selective aqueous leach of the catalyst would enable recovery of the PGM without generation of large volumes of

hazardous waste. Research in this area was performed by the U.S. Bureau of Mines (USBM) as part of its mission to provide an adequate supply of minerals to the Nation at an acceptable social, environmental, and economic cost.

Over the past 5 years, the Reno Research Center of the USBM has developed an autoclave cyanide leaching process for treatment of spent automobile catalytic converters (2-3). These catalysts usually contain Pt, Pd, and Rh, on a high-surface-area ceramic support. Operating in countercurrent flow, the USBM process uses three stages of leaching, with 1 pct cyanide addition at each stage, followed by several stages of repulp washing. The PGM are recovered from solution by thermal decomposition at 275 °C, which also results in the destruction of the complexing cyanide to levels below 0.2 mg/L. The cyanide leaching process typically recovers 90 pct of the Pt and Pd, and 80 pct of the Rh. From this experience, it was believed that the cyanide processing method could also be applied to petroleum catalysts. Several petroleum catalyst reprocessing companies were contacted regarding the cyanide leaching process. One of these companies, Gemini Industries of Santa Ana, CA, showed an interest in the process, and provided three samples of zeolite-supported petroleum refining catalyst for testing.

EXPERIMENTAL

MATERIALS

The petroleum catalyst samples received from Gemini Industries were in the form of small cylindrical pellets, about 3 mm in diameter by 5 mm long. The samples were split, sampled, and assayed to measure the PGM content. Samples 1, 2, and 3 contained 4,320, 4,350, and 7,060 g/t Pd, respectively. Platinum and rhodium were not detected. See table 1 for complete sample analysis. Catalyst sample 1 was also analyzed by X-ray diffraction methods to determine the composition of the matrix. X-ray diffraction showed that the matrix was a zeolite, faujasite, which is commonly used for fluid catalytic cracking catalysts. Faujasite has a chemical composition of $\text{Na}_2\text{Al}_2\text{Si}_4\text{O}_{12} \cdot 8\text{H}_2\text{O}$ (4). Pure faujasite should contain 8.4 pct Na, 9.8 pct Al, and 20.5 pct Si, but chemical analysis and X-ray fluorescence showed that the catalyst samples contained higher levels of aluminum and silicon, and much lower levels of sodium. The ion-exchange properties of zeolites are well

documented, and this provided an explanation for the differences in the analyses given above. The catalysts must have been treated with acid, in which case, hydrogen ions (H^+) would have been exchanged for sodium ions (Na^+) in the zeolite, leaving a sodium-deficient structure. Owing to the much lower atomic weight of hydrogen relative to sodium, the aluminum and silicon levels would be significantly increased above those for pure faujasite.

The surface area of sample 1 was measured by BET⁴ nitrogen adsorption, and a value of 300 m²/g was determined. This indicated significant surface area and porosity, as would be expected for a zeolite structure.

PROCEDURES

Atmospheric cyanide leaching tests were performed in a 1-L glass resin kettle. A 50-g sample of catalyst was added to 500 mL of leach solution in the kettle. Because of the high surface area of the catalyst, and the presence

³Italic numbers in parentheses refer to items in the list of references at the end of this report.

⁴BET stands for Brunauer, Emmett, and Teller, who originated this technique for measurement of surface area.

of Pd on the surface of the catalyst, leaching was conducted using uncrushed catalyst pellets. Leach solutions generally contained 1 pct NaCN (sodium cyanide) and 0.1M NaOH (sodium hydroxide) to ensure high alkalinity. Because of the large size of the catalyst pellets, it was impractical to agitate the pulp mechanically, but hand stirring was done periodically to homogenize the solution. Ten-milliliter samples of solution were removed at selected time intervals to measure the rate of leaching. At the conclusion of the test, the kettle was opened and the solids were filtered and washed to remove solubilized Pd. The pregnant and wash solutions were diluted to a known volume and analyzed by inductively coupled plasma (ICP) atomic emission spectroscopy. The leach residues were dried, weighed, and assayed by fire assay methods.

Table 1.—Petroleum catalyst sample characterization

(Percent unless otherwise specified)

Element	Sample 1	Sample 2	Sample 3
PGM, g/t			
Pd	4,320	4,350	7,060
Pt	<3	<3	<7
Rh	<3	<3	<7
WHOLE ROCK ELEMENTS			
Al	17	19	17
Ca	0.03	<0.02	0.14
Fe	0.11	0.13	0.23
K	0.25	0.22	<0.42
Mg	<0.02	<0.015	0.24
Na	0.010	0.54	0.79
Si	27	23	24
OTHER ELEMENTS			
Ag	<0.001	0.014	0.019
C	1.38	2.63	0.41
Co	0.01	0.010	0.009
Mo	0.04	0.13	0.13
Ni	0.004	0.20	0.05
Pb	0.01	0.10	0.11
V	0.002	<0.004	0.019

Small-scale pressure leaching tests were performed in a 250-mL-capacity Berghoff autoclave lined with Teflon

fluorocarbon polymer. Typically, 50 g of uncrushed catalyst was added to 100 mL of solution containing 1 pct NaCN and 0.1M NaOH. The pulp was sealed in the autoclave and heated to the target temperature. The autoclave was held at temperature for 1 h, the heat was shut off, and the autoclave was cooled. The heating and cooling steps each generally took about 1 h. The autoclave was then opened, and the solids were filtered and washed to remove solubilized Pd. The solution and solids were sampled for Pd assay. Larger scale leaching tests were run in a 2-L stainless steel Parr autoclave under similar conditions.

The ion-exchange capacity of catalyst sample 1 was measured by contacting the catalyst with sodium-bearing solutions and assaying the sodium content of the treated solution by atomic absorption (AA) spectroscopy. The effect of solution alkalinity was tested by preparing three different sodium-bearing solutions. Solutions were made up to equivalent sodium concentrations using NaCl (sodium chloride), Na₂CO₃ (sodium carbonate), and NaOH. Each solution was contacted with weighed catalyst samples at three different liquid-to-solid phase ratios to generate a loading curve.

Palladium precipitation tests were run in a 2-L stainless steel Parr autoclave. The primary variable in the precipitation process was temperature. Tests were run from 200 to 275 °C, in 25 °C increments. After the specified time at temperature, usually 1 h, the heater was shut off and the autoclave allowed to cool overnight. The contents were filtered and the solution was analyzed for Pd.

The catalyst head samples and selected leach residues were analyzed for waste disposal classification by the Federal Toxicity Characteristics Leaching Procedure (TCLP) (5) and California Waste Extraction Test (WET) (6). In these methods, a weighed quantity of residue is contacted with a weak acid solution. After a specified time, the solution is filtered and analyzed for certain toxic elements. The Federal test uses acetic acid solutions, while the California test employs citric acid solutions. If the concentration of the toxic elements in the test solution is less than a given standard, the material is classified as non-hazardous and can be disposed of in a landfill.

RESULTS AND DISCUSSION

LEACHING TESTS

Initially, only one sample of catalyst was received from Gemini Industries. Samples 2 and 3 were received from Gemini later in the research program. Therefore, most of the research concerning the effects of leaching parameters was done on sample 1. Table 2 shows leaching test results for sample 1. Temperature was the first variable tested.

In tests 1 and 2, leaching was conducted at temperatures of 23 °C (ambient) and 60 °C, respectively, with solutions containing 1 pct NaCN and 0.1M NaOH. The solutions were sampled at various time intervals during leaching to determine the leaching rate. Although the leaching rates were initially rapid, they leveled off after about 4 h. This resulted in overall Pd extractions after 24 h of 33 pct at 23 °C and 63 pct at 60 °C. The effect of longer leaching

time was measured in test 3, where the catalyst was leached for 14 days at ambient temperature. Palladium recovery increased to 45 pct in this case. These results indicated that leaching at either temperature under atmospheric pressure was not aggressive enough to quickly and completely dissolve the Pd. Therefore, the investigation turned to higher temperature leaching in an autoclave.

Table 2.—Leaching results—catalyst sample 1

Test	Temp, °C	Other test conditions ¹	Residue, g/t Pd	Pd ext, pct
ATMOSPHERIC LEACHING				
1	23	24 h, 10:1 L/S	2,670	33
2	60	24 h, 10:1 L/S	1,440	63
3	23	14 day, 10:1 L/S	2,260	45
AUTOCCLAVE LEACHING				
4	100		1,710	59
5	120		1,710	59
6	140		1,440	66
7	160		790	81
8	180		1,010	76
9	160	2 leaching stages	610	86
10A . . .	160	NaCN injection	710	83
10B . . .	160	NaCN injection	430	90
11	160	0.5M NaOH, 1.8:1 L/S . .	820	80
12	160	1.0M NaOH	810	80
13	160	5:1 L/S	790	81
14	160	Potassium salts	1,490	65
15A . . .	160	1.0M NaOH pretreatment	450	90
15B . . .	160	1.0M NaOH pretreatment	160	96
15C . . .	160		250	94

L/S Liquid-to-solid.

¹All tests were conducted for 1 h at the indicated temperature, with 0.1M NaOH, 1 pct NaCN solution, at a 2:1 L/S phase ratio, except as noted.

Tests 4 through 8 show the effect of increasing temperature on Pd extraction in autoclave leaching. An increase in temperature, up to 160 °C, gave improved Pd extraction, due to an increase in the dissolution rate. However, Pd extraction dropped off at 180 °C. Earlier research with automobile catalysts also showed optimum extraction at 160 °C (2). At higher temperatures, it appears that the Pd-cyanide complex begins to dissociate owing to hydrolysis of cyanide.

The effect of a second stage of leaching was also tested. In test 7, an extraction of 81 pct was obtained by leaching at 160 °C for 1 h with 1 pct NaCN and 0.1M NaOH. In test 9, two separate stages of leaching were run under these conditions on a fresh sample of catalyst. This resulted in a combined extraction of 86 pct. It may be that another stage of leaching could recover an additional 3 to 5 pct Pd. In the treatment of spent automobile catalytic converters, three stages of leaching have been found to be the optimum (2). A significant amount of Pd still remained in the zeolite residue; however, it has been

observed with automobile catalysts that recovering the last 5 to 10 pct of the PGM is difficult, no matter how extreme the test conditions become. This is probably due to the fact that PGM becomes locked in the pore structure of the catalyst as it degrades during use and is therefore inaccessible to the leaching solution. Further size reduction would not be practical, since ultrafine grinding would be required, and the costs of the grinding and the subsequent liquid-solid separation step would far outweigh the benefit of the small additional PGM recovery. The only way to recover the remaining PGM would be to destroy the pore structure by digestion or melting, but again, this would not be economical.

Another two-stage leaching test was run on the catalyst in tests 10A and 10B. The purpose of this test was to measure the effect of NaCN solution injection into the autoclave while at the leaching temperature. Because of hydrolysis of cyanide at elevated temperatures, the cyanide concentration is typically 10 pct of the original concentration by the time the operating temperature of 160 °C is reached. Injection of cyanide into the autoclave would present a higher cyanide concentration to the catalyst while at temperature than in any of the previous tests. Assay of the leach residue, after two stages of leaching with cyanide injection, showed 430 g/t. This gave 90-pct recovery, which is only slightly higher than was found for the earlier two-stage leach in test 9. The slight increase in recovery indicated that cyanide concentration was not a limiting factor in the autoclave leaching of the catalyst, as performed in these experiments. However, the injection procedure could be used repeatedly in a single stage of leaching over the course of several hours to give the same effect as three separate stages of leaching. This would save the time and expense of separate heating, cooling, filtering, and handling steps. This concept has been shown to be effective in the treatment of automobile exhaust catalysts (3).

In the course of the autoclave leaching test work, it was observed that the pH's of the pregnant leach solutions were in the range of 5 to 6. This was a significant decrease from the pH of the initial 0.1M NaOH solution, theoretically pH 13. The pH shift could present a safety hazard because toxic hydrogen cyanide (HCN) gas is more readily evolved from cyanide solutions as the pH is decreased. Much of the cyanide is destroyed by hydrolysis during the leaching period, but up to 500 mg/L free cyanide can remain in the solution after leaching at 160 °C. The pH shift was not observed in the atmospheric leaching tests. One major difference between the two test groups was that the liquid-to-solid phase ratio was decreased from 10 to 1 in atmospheric leaching to 2 to 1 in autoclave leaching. The phase ratio was decreased because intermediate sampling was not done in autoclave leaching and because less reagent was required. However,

it appeared that the decreased solution volume had affected the final pH of the solution. The ion-exchange properties of zeolites are well known, and further research showed that this was probably the cause of the pH shift. The zeolite must have been previously contacted with acid, which would result in exchange of H^+ ions for Na^+ ions in the mineral structure. This was confirmed by chemical analysis of the as-received zeolite sample, which showed that the catalyst was deficient in sodium. When the zeolite came into contact with alkaline leaching solutions, the equilibrium was reversed and H^+ ions were released to solution in exchange for Na^+ ions. The decrease in the phase ratio significantly decreased the total amount of NaOH available from solution. Sodium exchange for H^+ neutralized the OH^- and resulted in a decrease in pH. Sodium analysis of the leach solutions confirmed the sodium depletion. In addition, ion exchange also explained the significant weight increase of the residue after leaching, up to 10 pct in some cases.

A series of ion-exchange tests was run to measure the tendency of the zeolite catalyst to exchange H^+ for Na^+ . Solutions of NaCl, Na_2CO_3 , and NaOH were prepared with equivalent sodium concentrations. Three different phase ratios were tested with each solution. The most sodium was adsorbed from the hydroxide solution, followed by the carbonate and the chloride solutions, respectively. This order parallels the alkalinity of the solutions and suggests that alkalinity is the primary factor. A typical cyanide leaching solution (1 pct NaCN, 0.1M NaOH), originally 0.3M in Na^+ , was depleted to less than 0.05M Na^+ at low liquid-to-solid ratios. In parallel with Na^+ depletion was a decrease in pH caused by exchanged H^+ .

The pK_a of HCN is 9.2 (7). This means that at pH 9.2, 50 pct of the total cyanide present is in the form of dissolved HCN, and 50 pct is in the form of ionic CN^- . As the pH increases above pH 9.2, the ratio of CN^- to HCN increases. Conversely, as the pH decreases below pH 9.2, the ratio of CN^- to HCN decreases. Toxic HCN gas can be evolved from solutions containing dissolved HCN, depending on the HCN concentration and the level of agitation. Therefore, cyanide leaching is usually undertaken at higher pH levels to ensure that most of the cyanide is in the ionic form, which cannot evolve HCN gas. For solutions containing up to 500 mg/L of free cyanide, the pH should be maintained at 12 or higher to minimize the potential for HCN volatilization. Further catalyst leaching tests were undertaken with the goal of increasing the equilibrium pH to minimize the safety hazard associated with HCN gas. In tests 11 and 12 in table 2, the NaOH addition was increased to 0.5 and 1.0M, respectively, to counteract the ion-exchange tendencies of the zeolite and give a higher equilibrium pH. In both of these cases, the pH after leaching was in the range of 8 to 9, but much more Na^+ had been adsorbed from solution. This was due to

the increased alkalinity of the solution, as was also observed in the ion-exchange tests. Palladium extraction was not affected by the increased caustic addition. Another approach to increase equilibrium pH was to increase the liquid-to-solid phase ratio to provide more caustic without increasing the alkalinity. Test 13 was run with a 5-to-1 phase ratio to counteract the ion exchange of the zeolite. In this case the equilibrium pH was 9, which was still somewhat low for safe handling of cyanide solutions. The Pd extraction was 81 pct in test 13, similar to previous tests.

Another approach was used in test 14, in which potassium salts were substituted for sodium salts at equimolar concentrations. Since zeolites in general have very well defined pore sizes, it was thought that the ion-exchange tendency could be inhibited by substituting the larger potassium ion for sodium. However, the equilibrium pH in this test was pH 5. This indicated that potassium was adsorbed at least as well as sodium, if not better. The Pd extraction in this test was decreased to about 65 pct, about 15 pct less than with sodium salts. Therefore, no further tests with potassium or other cations were attempted.

Another method to counteract the ion exchange of the zeolite was tried in test 15A. In this case, the zeolite was pretreated with a 1.0M solution of NaOH at a phase ratio of 5 to 1, filtered, then leached at 160 °C with the standard leaching solution containing 0.1M NaOH and 1 pct NaCN. The final pH in this test was pH 12. The Pd recovery in this test was 90 pct, which was an improvement over earlier single-stage leaching results. About 10 pct of the Pd was extracted by the NaOH pretreatment solution, which was found to contain about 100 mg/L of Pd. This may be due to the presence of Pd salts on the catalyst or to the formation of some soluble Pd species under the strongly alkaline conditions of the pretreatment. Preliminary tests with the pretreatment solutions showed that a decrease in pH to 12 or less resulted in precipitation of the solubilized Pd. It may be possible to use a countercurrent pretreatment scheme where fresh catalyst would be contacted with spent pretreat solution to precipitate the Pd and neutralize the excess NaOH. Further testing will be necessary to work out the details of the countercurrent process. The pretreatment step with 1.0M NaOH appears to be necessary to avoid pH decreases due to ion exchange by the catalyst. Additional leaching tests were carried out on the test 15A residue. Two options were examined: in test 15B, the residue was again contacted with 1.0M NaOH, followed by an additional stage of leaching, and in test 15C, the residue was subjected to an additional cyanide leaching stage without pretreatment. The results shown in table 2 indicate that the second pretreatment step was unnecessary, and that an additional leach increased Pd extraction to 95 pct.

Two additional catalyst samples were received at this point. Several leaching tests were run on each sample, and the results are given in tables 3 and 4. For sample 2, a single stage of leaching, test 1, gave 42 pct Pd recovery (see table 3), which was much less than for sample 1, at 81 pct Pd recovery. As with sample 1, the pH of the pregnant leach solution was in the range of 5 to 6. This demonstrates a similarity with sample 1, although this sample appears to be more refractory. The two-stage leach, tests 2A and 2B, with NaOH pretreatment boosted recovery to 87 pct, compared with 94 pct for sample 1. In tests 3A and 3B, sample 2 was subjected to NaOH pretreatment, followed by autoclave leaching with three injections of NaCN while at temperature. This treatment gave 87 pct Pd recovery, and one additional separate stage of leaching boosted that to 92 pct final recovery.

Table 3.—Autoclave leaching results—catalyst sample 2

Test	Temp, °C	Other test conditions ¹	Residue, g/t Pd	Pd ext, pct
1	160		2,460	42
2A . . .	160	1.0M NaOH pretreatment . .	880	79
2B . . .	160		560	87
3A . . .	160	Pretreatment, NaCN injection	550	87
3B . . .	160		330	92

¹All tests were conducted for 1 h at the indicated temperature, with 0.1M NaOH, 1 pct NaCN solution, at a 2:1 L/S phase ratio, except as noted.

Table 4.—Autoclave leaching results—catalyst sample 3

Test	Temp, °C	Other test conditions ¹	Residue, g/t Pd	Pd ext, pct
1	160		3,140	56
2A . . .	160	1.0M NaOH pretreatment . .	2,080	68
2B . . .	160		1,580	76
3A . . .	160	Pretreatment, NaCN injection	1,480	77
3B . . .	160		1,390	78

¹All tests were conducted for 1 h at the indicated temperature, with 0.1M NaOH, 1 pct NaCN solution, at a 2:1 L/S phase ratio, except as noted.

As shown in table 4, sample 3 proved even more refractory. Test 1 shows a Pd recovery of 56 pct after a single stage of autoclave leaching. As with the other catalyst samples, the leach solution pH decreased significantly over the course of the experiment. The two-stage leach with NaOH pretreatment, tests 2A and 2B, gave 76 pct recovery. Pretreatment followed by autoclave leaching with three injections of NaCN gave a comparable 77 pct Pd recovery, and one final releach of that residue gave a final recovery of 78 pct of the Pd, tests 3A and 3B. Unfortunately, sample 3 was not only the most refractory of the

samples tested, it was also the highest grade material, assaying 7,060 g/t (0.7 pct) Pd. Thus, a leaching recovery of 78 pct of the Pd still left 1,390 g/t Pd in the residue, a fairly high value of Pd.

The reason for the greater refractoriness of samples 2 and 3 is not known for certain, but is probably related to the conditions of service and regeneration that the material was exposed to during its operating lifetime. Specimens of sample 3 catalyst head and leach residue were examined with a scanning electron microscope, coupled with an X-ray fluorescence microprobe. The purpose of this examination was to determine whether the unleached Pd was locked in the zeolite matrix or otherwise unavailable for dissolution. However, no Pd was detected in either sample, although the catalyst head sample contained 0.7 pct Pd. The Pd in the catalyst samples is evidently so finely distributed as to be undetectable by the instrument. If sample 3 is truly representative of the material available for reprocessing, the high-temperature cyanide leaching process may not be the best available technology for treatment. If, however, samples 1 and 2 are more representative, the process could be attractive because of the higher Pd recovery obtained for these samples. An industry survey will be required to answer these questions.

SOLID WASTE CHARACTERIZATION ANALYSIS

An important consideration in the processing of solid materials is disposal of the residue after treatment. If the residue is classified as a hazardous waste, the disposal costs could render the entire process uneconomic. Therefore, catalyst samples were analyzed by both the Federal and California waste analysis methods, both before and after leaching. The Federal test is known as the TCLP method, while the California test is called the WET method (5-6). These procedures are briefly described in the experimental section of this report. The results of the Federal TCLP tests are given in table 5. All of the catalyst head samples passed the TCLP tests. Table 6 shows the results for the WET tests. Only one sample failed the WET test. This was the untreated catalyst sample 2, which failed for the elements Mo and Ni. However, these elements were partly extracted during the leaching process, so that the sample 2 leach residue passed the WET test. In summary, the solid waste characterization tests indicate that all catalyst leach residues would be acceptable for landfill disposal, under both the Federal and California State requirements.

Pd RECOVERY FROM SOLUTION

The most promising method for recovery of PGM from automobile exhaust catalyst leaching solutions was thermal decomposition of cyanide complexes in an autoclave at

275 °C (2). Other techniques, such as cementation, ion exchange, solvent extraction, carbon adsorption, and electrowinning, were tested and were found to be inadequate, usually because of incomplete removal of PGM from solution. In the thermal decomposition treatment, the hydrolysis of cyanide at elevated temperatures resulted in destabilization of the PGM complex, with the result that the PGM were precipitated. The hydrolysis of cyanide also resulted in the formation of the formate ion (HCOO^-) and ammonia. An additional benefit of this method was that the free cyanide concentration in the barren solution was usually decreased to less than 0.2 mg/L, which is a common discharge limit for cyanide.

Table 5.—Toxicity characteristics test results, Federal TCLP procedure, milligrams per liter

Element	Maximum allowable concentration	Catalyst head sample		
		1	2	3
Ag	5	<0.012	0.078	0.088
As	5	<0.048	0.94	1.2
Ba	100	0.049	0.17	0.12
Cd	1	<0.004	0.10	0.10
Cr	5	0.062	<0.10	<0.10
Hg	0.2	<0.002	<0.0012	<0.0012
Pb	5	<0.06	0.87	<0.22
Se	1	<0.006	<0.010	<0.010

It was observed in treatment of automobile catalysts that Pd was the first cyanide complex to be decomposed as the temperature increased, followed by Rh and Pt (2).

Since the petroleum catalyst leach solutions contained only Pd, temperatures lower than 275 °C might be sufficient to recover all of the Pd. A series of precipitation tests was run to investigate the temperature effect, from 200 to 275 °C, at 25 °C intervals. In each test, the solution was brought up to temperature, held at the target temperature for one or more hours, and cooled overnight. The Pd removal efficiency of the treatment was calculated by using the analysis of the barren solution after filtration. Test results are shown in table 7. As expected, it was found that temperatures below 275 °C were sufficient for complete precipitation when Pd was the only PGM present in the liquor. The Pd content of the barren solution was less than 0.6 mg/L after 1 h of treatment at temperatures of 225 °C and above. The precipitate was a black powder assaying over 50 pct Pd. The barren solutions were also assayed for free and total cyanide content, as shown in table 7. At 225 °C, the total cyanide content after thermal decomposition treatment was 0.7 mg/L, which was higher than the typical discharge limit of 0.2 mg/L. The total cyanide content was found to be less than 0.2 mg/L when precipitation was conducted at temperatures of 250 °C and above. Steam pressure increases rapidly with temperature in this range: from 2.5 MPa (370 psia) at 225 °C, to 4.0 MPa (577 psia) at 250 °C, and to 5.9 MPa (862 psia) at 275 °C. Therefore, in terms of the capital cost of the autoclave, the most economical alternative would be the lowest temperature that meets the requirements of the flowsheet. This is 250 °C for 1 h, where both the Pd and cyanide contents were below the required limits.

Table 6.—Toxicity characteristics test results, California WET procedure, milligrams per liter

Element	Maximum allowable concentration	Catalyst head sample			Leach residue		
		1	2	3	1 ¹	2 ²	3 ³
Ag	5	<0.01	0.15	0.53	<0.01	0.60	0.65
As	5	<0.054	<1.5	<1.5	<0.04	<0.3	<1.5
Ba	100	0.23	0.35	0.54	0.27	0.55	0.07
Be	75	<0.005	<0.005	<0.005	<0.005	<0.001	<0.005
Cd	1	<0.003	0.081	0.17	<0.003	0.18	0.21
Co	80	3.6	2.5	1.2	0.20	1.4	0.32
Cr	5	0.13	0.04	0.05	0.10	<0.02	0.089
Cu	25	0.27	<0.05	1.6	<0.009	1.6	0.57
F	180	<1.0	<10	<10	<1.0	<10	<10
Hg	0.2	<0.006	<0.0012	<0.0012	<0.006	<0.0012	<0.0012
Mo	350	24	490	70	2.8	70	2.6
Ni	20	2.3	45	4.6	0.31	4.8	1.1
Pb	5	0.81	1.5	4.2	<0.06	4.0	3.8
Sb	15	<0.11	<0.35	0.92	0.08	0.55	<0.35
Se	1	<0.006	<0.010	<0.010	<0.006	<0.01	<0.01
Ti	7	<0.001	<1.0	<1.0	<0.001	<1.0	<1.0
V	24	0.08	0.44	1.2	0.02	1.0	0.79
Zn	250	1.21	0.72	5.9	0.52	5.6	6.3

¹Residue from test 9, table 2.

²Residue from test 3A, table 3.

³Residue from test 3A, table 4.

Table 7.—Precipitation of Pd from leach solution

Sample	Temp, °C	Time, h	Concentration			
			Pd, mg/L	CN ⁻ _{free} , mg/L	CN ⁻ _{tot} , mg/L	CO ₃ ²⁻ , g/L
Feed			425	280	450	1.2
Test 1	200	1	263	<0.01	210	1.1
Test 2	225	1	<0.6	<0.01	0.73	1.1
Test 3	250	1	0.6	<0.01	0.046	1.3
Test 4	275	1	0.9	<0.01	<0.015	1.4
Test 5	275	2	<0.6			

CONCLUSIONS

The treatment of Pd-bearing, zeolite-based, petroleum processing catalysts by cyanide leaching has been examined. For the initial sample received, ambient temperature leaching with 1 pct NaCN, even after 14 days, resulted in only 45 pct extraction of the Pd. When the temperature was increased to 60 °C, extraction was still only 65 pct after 24 h. These results showed that leaching at temperatures below 100 °C and at atmospheric pressure dissolved an unacceptable percentage of Pd. The investigation turned toward higher temperature leaching in an autoclave.

A series of autoclave leaching tests was conducted using 0.1M NaOH and 1 pct NaCN solutions at temperatures between 100 and 180 °C. The optimum temperature for Pd extraction was found to be 160 °C, where 80 pct of the Pd was extracted with a single stage of leaching. Two stages of leaching gave 86 pct extraction of the Pd. Another stage of leaching may result in an additional 2 to 3 pct extraction.

The zeolite-based catalyst exhibited a strong capacity for ion exchange, especially under alkaline conditions. This resulted in a significant pH shift as the released hydrogen ions neutralized the hydroxide in solution. Since toxic HCN gas is more readily evolved from cyanide solutions at lower pH's, this situation should be avoided. Several alternatives were tested for counteracting the ion exchange of the catalyst. A tenfold increase in NaOH concentration increased the equilibrium pH slightly, but much more sodium was adsorbed. Increasing the phase ratio to 5 to 1 also helped increase equilibrium pH, but again, not to an acceptable level. Substitution of

potassium salts for sodium salts had no effect on the pH shift and decreased extraction. The best alternative was pretreatment with 1M NaOH solution. Following the NaOH pretreatment, two stages of leaching with solution containing 1 pct NaCN and 0.1M NaOH gave 95 pct Pd recovery. An unforeseen consequence of the caustic pretreatment was the dissolution of about 10 pct of the Pd content. Countercurrent multistage leaching is the best prospect for pretreatment of the catalyst and recovery of Pd from the pretreat solution.

The process was tested on two additional catalyst samples received later in the research program. These samples proved to be more refractory, giving 92 and 78 pct recovery after NaOH pretreatment and two stages of leaching. A market survey may be appropriate to determine which catalyst types are most prevalent.

The catalyst head samples and leach residues were analyzed to determine whether they would be classified as hazardous waste or could be disposed of in a landfill. All leached residues passed both the Federal and California tests, indicating that landfill disposal would be acceptable.

The optimum temperature for thermal precipitation of Pd from the leach solution was found to be 250 °C. Although Pd removal was complete after 1 h at 225 °C, the total cyanide concentration was still above the typical discharge limit of 0.2 mg/L. After 1 h at 250 °C, the barren solution from thermal decomposition assayed less than 1 mg/L Pd and less than 0.2 mg/L total cyanide. The precipitation product was a black powder assaying over 50 pct Pd.

ACKNOWLEDGMENT

The authors gratefully acknowledge the contribution of Gemini Industries of Santa Ana, CA, in providing the test samples.

REFERENCES

1. Thayer, A. M. Catalyst Suppliers Face Changing Industry. *Chem. & Eng. News*, v. 70, No. 10, Mar. 9, 1992, p. 28.
2. Desmond, D. P., G. B. Atkinson, R. J. Kuczynski, and L. A. Walters. High-Temperature Cyanide Leaching of Platinum-Group Metals From Automobile Catalysts—Laboratory Tests. USBM RI 9384, 1991, 8 pp.
3. Kuczynski, R. J., G. B. Atkinson, and W. J. Dolinar. High-Temperature Cyanide Leaching of Platinum-Group Metals From Automobile Catalysts—Pilot Plant. USBM RI 9543, 1995, in press.
4. Gottardi, G., and E. Galli. *Natural Zeolites*. Springer-Verlag, New York, 1985, p. 336.
5. Federal Register. U.S. Environmental Protection Agency. Identification and Listing of Hazardous Waste. V. 55, No. 61, Mar. 29, 1990, pp. 11862-11875.
6. Barclays California Code of Regulations. Criteria for Identification of Hazardous and Extremely Hazardous Wastes. Register 90, Nos. 38-41, Oct. 12, 1990, pp. 678-681.
7. Cotton, F. A., and G. Wilkinson. *Advanced Inorganic Chemistry*, 4th ed. Wiley, New York, 1980, p. 369.